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Lockheed Missiles and Space Co, Inc, Palo Alto, Calif

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Cincinnati OH 45268

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Summary Report

Detoxification of Navy Red Dye by Microwave Plasma

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Summary Report

DETOXIFICATION OF NAVY RED DYE BY MICROWAVE PLASMA

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CINCINNATI, OHIO 45268

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This report describes a successful detoxification by microwave plasma of a particularly refractory U.S. Navy red dye mixture which is used in pyrotechnic smoke compositions. The reactions produced harmless gases, and no carcinogens or other toxic materials in the process effluent. During the study, various unit operations and processes were evaluated to determine efficiency and the potential for future expansion.

Francis T. Mayo
Director
Municipal Environmental Research Laboratory

PREFACE

Toxic organic substances, such as chlorinated hydrocarbons, and many organonitrogen, organophosphorous, and organometallic compounds are components of pesticides which have been withdrawn from use, are obsolete, or are constituents of hazardous military or industrial wastes. These materials must be managed or disposed of safely and effectively. A primary responsibility of the U.S. Environmental Protection Agency's Solid and Hazardous Waste Research Division (SHWRD) has been to encourage and support research and development efforts in the area of hazardous waste disposal technology. For compounds of nominal toxicity, laudable achievements have been accomplished in the technology of thermal destruction, chemical and biological detoxification, and special landfill methods. However, with the exception of high-cost incinerator processing, little or new technology has been developed for the disposal of highly toxic or extremely persistent wastes. These materials are described in the 1974 EPA Report to Congress, Disposal of Hazardous Wastes, SW-115.

As part of a continuing program to evaluate the newly developed microwave plasma process on toxic materials of current interest, a U.S. Navy red dye pyrotechnic smoke mixture was selected for detoxification because of the refractory, or difficult to decompose, behavior of the two potentially carcinogenic dyes which constitute a major portion of this mixture.

ABSTRACT

The process of microwave plasma detoxification has been applied successfully to the destruction/disposal of a U.S. Navy red dye pyrotechnic smoke mixture. The mixture was added as a powder, a solvent solution, and a water slurry.

Material balance for detoxification of the slurry indicated that less than 0.20 percent solids were found beyond the reaction zone, or 99.8+ percent conversion to gaseous products. Analysis by spectrophotometry in the visible region indicated little or no dye starting materials (< 5 ppm) in the residue. Ultraviolet fluorescence, UV spectrophotometry, and gas chromotography/mass spectrometry indicated the presence of less than 2 ppm carcinogenic polyaromatic hydrocarbons (PAH). Since PAH has been found in air oxidation products derived from these materials, a significant advantage would appear to derive from the plasma process.

During the study, several vacuum feed techniques were evaluated with a view toward their utilization in forthcoming pilot equipment tests. Especially with high solids slurries and solutions, where non-Newtonian flow can cause difficulties when gravity feed methods are used, it will be necessary to use positive displacement methods to obtain uniformity and reproducibility during the addition process.

Further work is suggested, using larger quantities of the mixture to optimize throughput and to calculate process costs for economic comparisons with other detoxification methods.

This report was submitted in partial fulfillment of Phase II of Contract 68-03-2190 by the Lockheed Palo Alto Research Laboratory of Lockheed Missiles & Space Company, Inc., under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period August 1976 – July 1977.

For work performed under Phase I, the report entitled, "Development of Microwave Plasma Detoxification Process for Hazardous Wastes," EPA-600/2-77-030, April 1977, may be consulted for additional details on the technique development.

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Appreciation is expressed to Dr. Carl E. Dinerman and Mr. James Short, Naval Weapons Support Center, Crane, Indiana, who foresaw the applicability of the microwave plasma process to detoxification of Navy dye compositions, supplied the dyes, and advised on pertinent analytical and handling procedures.

The Project Officer for the Environmental Protection Agency was Mr. Donald A. Oberacker, whose advice and guidance are sincerely acknowledged.

SECTION 1

INTRODUCTION

During 1975 – 1976, based on an EPA supported study, the process of microwave plasma decomposition of organic and organometallic compounds was applied successfully to the detoxification/destruction of highly toxic wastes.[1] The effectiveness of an expanded scale plasma was evaluated using hazardous organic materials of current interest. The products of these reactions were identified in order to estimate their toxicity and to determine the potential for recycling or recovery of useful by-products. The program resulted in an expansion of the state-of-the-art in microwave plasma detoxification from 1 to 5 g/hr in the original laboratory apparatus to 3 kg/hr (7 lb/hr) in the larger system. This scale-up changed the perspective from one of academic interest to that of a realistic or practical level.

As a result of successful detoxification, more complex, real-world mixtures were suggested for continued process testing and evaluation. Such a material was obtained from the Naval Weapons Support Center (NWSC), Crane, Indiana. As a colored smoke, these materials were considered important for disposal because of the presence of carcinogenic or suspected carcinogenic dyes in the smoke mixture.[2] The results of a study of the detoxification of this mixture are presented in the sections which follow.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The process of microwave plasma decomposition was used successfully to detoxify a U.S. Navy dye mixture to harmless gases and solids. The rate of addition in this initial study was 500 g/hr of aqueous slurry which contained 15 percent solids. The process, in its current state of development, required drop-feed (gravity) addition to the plasma zone. Decomposition was complete; very little or no starting material was found in a small amount of solid product and no significant quantities of polyaromatic hydrocarbons were detected, according to UV absorption, UV fluorescence, IR spectroscopy, and GC/MS.

Further work is recommended to improve the methods of addition to maximize material throughput, and should include testing of total smoke mixtures containing the potassium chlorate oxidizer component. It is also recommended that detoxification be carried out in the 15-kW plasma system now under construction, whereby positive feed techniques would be used for solids as well as aqueous slurries.

Work on other toxic waste materials of interest to the Navy is also suggested. These include shipboard hazardous chemicals, outdated disinfectants, organometallic compounds from munitions, and certain pesticides originally used to clear bird-attracting insects from airfields. The use of portable microwave plasma detoxification equipment would, in addition, result in a significant diminution in time and labor now required for the transportation of these materials to incinerators, where permitted, or to regulated toxic waste disposal sites when necessary.

SECTION 3

MATERIALS

The smoke composition selected is contained in a Navy inventory material known as MK 13 Mod O Marine Smoke and Illumination Signal. This material accounted for approximately 70 percent of the 9300 kg excess to be disposed of by the Navy. The composition contained 1-methylanthraquinone and xylene-azo-β-napthol dyes, which appear red in powder form. The components, excluding the potassium chlorate oxidant, are listed in Table 1. The $KClO_3$ was omitted since it can be removed from mixtures by water extraction.[3] In addition, its inclusion, initially, would result in the formation of nonuniform, and therefore, detrimental gas expansions in the reactor, which would confound the initial data. The $KClO_3$ component should, however, be investigated later as part of the mixture, pending approval of the need for further study.

The reactant gas was 99.5 percent minimum purity industrial grade oxygen, Federal Spec. BB-O-925(a), Type I, in which the 0.5 percent nonoxygen components were approximately 0.05 percent nitrogen, the remainder being argon and other gases in trace amounts. Other specific one-time use materials are listed in the sections in which they are applied.

TABLE 1. COMPOSITION OF SMOKE COMPONENT OF THE MK 13 MOD O MARINE SMOKE AND ILLUMINATION SIGNAL

Components in Powder Mixture*	Amount (%)
Xylene-azo-β-naphthol	55.4
1-Methylaminoanthraquinone	18.9
Sucrose	18.0
Graphite	1.8
Silica Binder	5.9
	100.0

*Excluding 18.9 percent $KClO_3$ oxidant. To convert to $KClO_3$ composition, multiply by the factor 0.811.

SECTION 4

MICROWAVE PLASMA SYSTEMS

4.1 MICROWAVE PLASMA CHARACTERISTICS

The characteristics associated with the microwave plasma detoxification process are detailed in Ref. 1 and, therefore, are presented in abbreviated form as follows.

A plasma or discharge is a partially ionized gaseous mixture consisting of free electrons, ions, and various neutral species. The free electrons are the principal initiators of the plasma reactions. When the electrons undergo inelastic collisions with the reactants, they cause either ionization, which produces more electrons and ions, or dissociation of the reactants into free radicals. These fragments, with their unpaired electrons, can then undergo a series of rapid reactions to the final products.

The free electrons are energized by the oscillating electric field produced by the microwave energy (2450 MHz) applied to the plasma. In this way, the electrons couple the electrical energy into the reactants and force them to undergo the desired reactions. The oscillating electric field produced by the microwaves changes polarity so rapidly that the charged species in the plasma reverse their direction of acceleration before they are swept to the walls of the container where they are likely to be destroyed. Therefore, the plasma can be maintained without the use of internal electrodes, which are usually required for plasmas operating at lower frequencies. Consequently, there are no difficulties with internal electrode decomposition from corrosive species in the plasma, which is a known problem with DC or arc discharges.

The plasma used in this investigation is operated at reduced pressure on the order of one to a few hundred torr. This permits the free electrons to be energized to achieve temperatures much higher than those of the neutral gases, since there are significantly fewer inelastic collisions occurring to cool the reactive electrons. The electrons simulate "temperatures" on the order of 10,000°K and higher, while the temperature of the neutral gas is less than 1,000°K. By operating under these nonequilibrium conditions, it is possible to maintain the free electrons at high temperatures without heating the bulk neutral gas, thereby conserving electrical energy. Since the plasma decomposition mechanism is principally electronic, rather than thermal, the microwave applicator-power coupling equipment can be maintained at relatively low temperatures. Thus, the materials of construction associated with furnaces or incinerator equipment are generally unnecessary, and maintenance expenses will be low. In addition, the systems are leak tight, and, therefore, safe, which is a result of the requirement for working at reduced pressures.

4.2 CHEMISTRY OF MICROWAVE PLASMA REACTIONS

In general, the decomposition of organic materials, including dyes, saccharides, etc., will encompass a large number of complex reactions. The primary step probably involves collisions between the compound and either free electrons or reactive species produced by the action of the discharge on the reactant gas. Through the action of electron collisions with other species, free radicals and atoms are produced from the organic compounds. These species then react further to form secondary products.

When oxygen is used as the reactant gas in the plasma, atomic oxygen becomes the primary reactive species which rapidly oxidizes the organic compounds introduced into the discharge. In addition, the large numbers of energetic free electrons continually bombard the compounds, and any remaining organic components will be broken up into smaller free radical fragments, which rapidly react with the oxygen present. The free electrons may also collide with the CO_2 produced, resulting in dissociation to CO and oxygen atoms.[4] Thus, an equilibrium concentration of CO and CO_2 may be present in the product effluent under conditions of complete oxidative conversion.

4.3 APPARATUS

The plasma system, designed and built according to Lockheed Palo Alto Research Laboratory (LPARL) specifications, consists of feed hardware, an oxygen supply, a plasma reactor tube, and an effluent-product sampling receiver and traps. A block diagram of the system and related components is shown in Fig. 1. A schematic diagram is detailed in Fig. 2. The microwave hardware was supplied by Gerling Moore, Inc., Palo Alto, CA. In Ref. 1, numerous photographs of the system can be seen, plus the identification of all components. Additional engineering and design detail are also provided for the reader interested in further information.

The applicator used was a dual trough waveguide in which each trough was fed by a 2.5-kW, 2450-MHz power source. The length of the applicator, exclusive of two 20.3-cm end-mounted radiation cutoff sections, was 41 cm. The reactor tubes were fabricated from transparent quartz with a 1.5-mm wall thickness, and an outside diameter of 48- to 50-mm liter. Quartz Raschig rings were used in order to increase the residence time of liquid and solid materials within the plasma zone. (Ring dimensions were 8 mm o.d. by 4 mm length and 8 mm by 8 mm.) The volume of the reactor was approximately 0.6 liter.

The vacuum pump was a Welch "Duo-Seal" Model 1397 oil-sealed two-stage mechanical pump with a free-air displacement of 425 liters/min. Dry ice-acetone and liquid nitrogen traps were installed between the reactor output and the pump for product collection, and to maintain cleanliness of the pump oil. The output from the pump was passed through a stack exhaust to the exit port on the roof of the building.

During operation of the microwave units, a Holaday Model HI 1500-3 microwave radiation monitor (Holaday Industries, Inc., Edina, Minnesota) and a Narda Model B86B3 radiation monitor (Narda Microwave Corp., Plainview, N.Y.) were used to monitor power leakage. Levels were less than 1 mW/cm^2 in the immediate vicinity of the apparatus, including the plasma discharge tube.

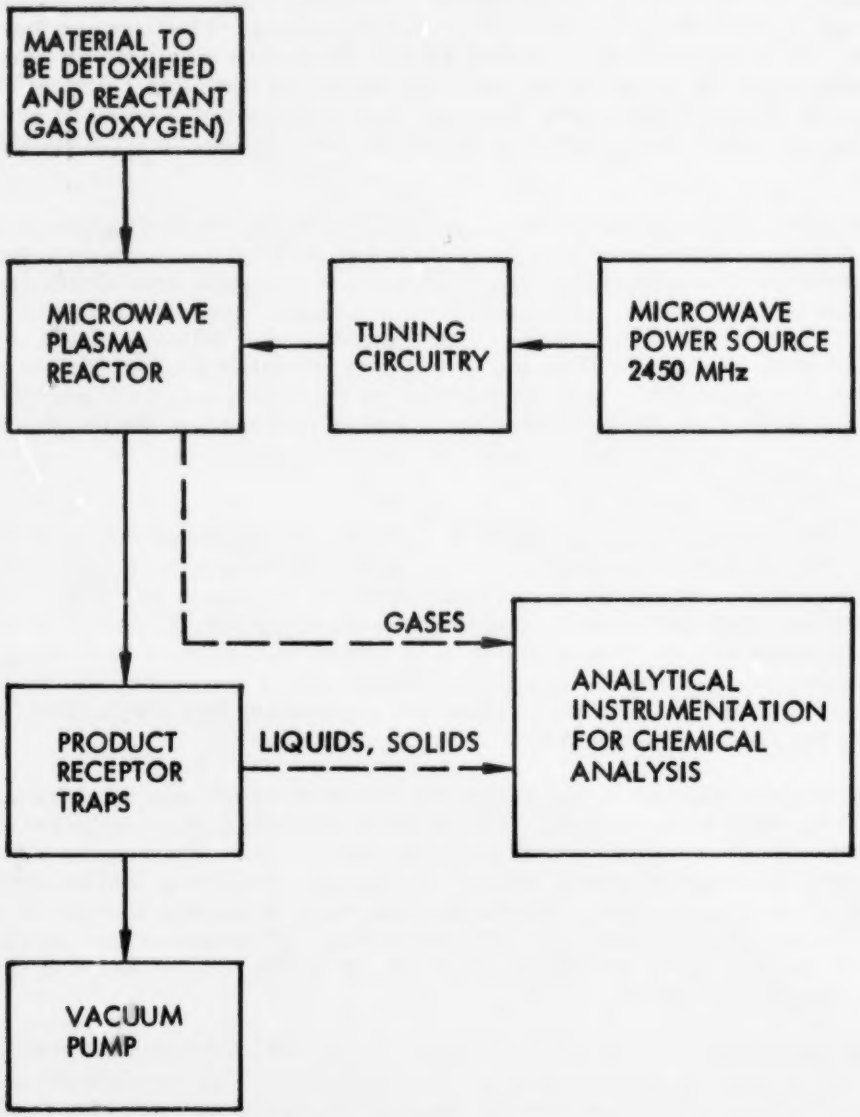

Figure 1. Block diagram of microwave plasma system and related components.

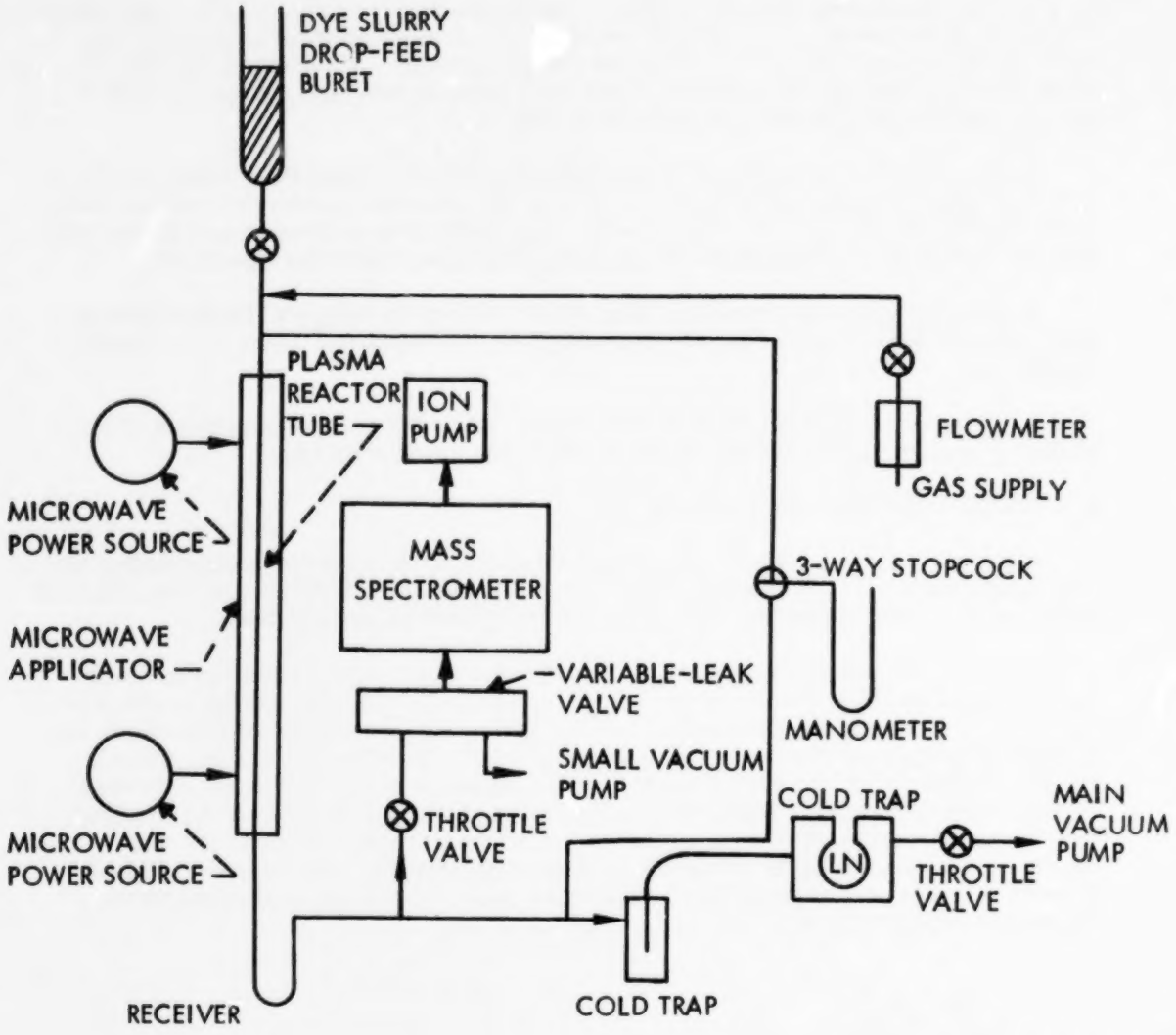

Figure 2. Schematic of expanded scale microwave plasma system.

4.4 ANALYTICAL PROCEDURES

Mass spectrometric (MS) analysis of the gases leaving the reactor were performed on a Varian Associates Model 974-0002 residual gas analyzer (quadrupole mass spectrometer) with a range of 250 atomic mass units. A small quantity of the gas was continuously pumped past a variable-leak sampling valve. The gases bled into the mass spectrometer by the sampling valve were pumped from the system by an ion pump. The sampling system is included in Fig. 2.

Infrared spectra of solid and liquid effluents collected from the product receiver and traps were determined on a Perkin-Elmer 621 infrared spectrophotometer with a range of 4000 to 400 cm^{-1} (2.5 to 25 μm). Materials to be analyzed were ground with KBr and compressed into pellets for scanning over the prescribed spectrum.

Visible and ultraviolet spectra from 200 to 700 nm on solid and liquid effluents were obtained on a Cary Model 14 Recording Spectrophotometer using conventional procedures.

A Finnegan Model 4021 GC/MS data system was used toward completion of the study for analysis of the polyaromatic dye decomposition products.

4.5 EXPERIMENTAL PROCEDURE

In general, the procedure was the same as that used in previous expanded-scale plasma reactions.[1] Certain modifications were required, however, as the result of differences in feed technique, and several are detailed in the Appendix.

Initially, the entire system was evacuated to about 1 torr. The pressure was then adjusted to about 10 torr by the addition of oxygen. The microwave power was then turned on to initiate the plasma. Additional oxygen was introduced to obtain the desired pressure and flow rate in combination with regulation by the main throttle valve. At this point, the tuning controls were adjusted to give minimum reflected power. After obtaining a background MS scan (reactant gas flowing minus material to be detoxified), a needle valve at the bottom of the dropping funnel in the case of liquids was opened to begin introduction of the dye mixture. The gaseous effluent from the plasma was sampled and analyzed by mass spectrometry several times during the course of a run.

SECTION 5

RESULTS

The experimental approach was to obtain maximum throughput, with the objective of achieving the lowest process costs. Generally, the total microwave power available was applied to the discharge. This allowed the plasma to operate at maximum pressure, thereby permitting a maximum amount of oxygen to be used as the plasma gas for reaction with the dye mixture.

The dye mixture was fed into the plasma system in several forms: as a methanol-water mixture, a methyl ethyl ketone solution, an aqueous slurry, and a powdered solid. Each of these materials was tested, but only the water slurry could be introduced uniformly and reproducibly to obtain reliable analytical data. This work is described from a chronological standpoint in the Appendix, and elucidates the problems as they developed and the solutions that were applied. The development of the successful water slurry feed technique and subsequent detoxification is described in the following subsections.

Of the several feed systems that were tested for the introduction of the dye mixture into the plasma zone, the aqueous dispersion technique was the most successful. The apparatus constructed for this application (Fig. 3) used the technology described in the Appendix, section A.4, with regard to development of dye dispersions in a water medium. Experimental results using this technique are described in the following paragraphs.

Since the red dye components, as a mixture, are essentially hydrophobic, TEC 1216E nonionic surfactant (TEC Chemical Co., Monterey Park, CA) ethylene oxide nonylphenol, was used to produce the required dispersions. The slurry was prepared from a 20 percent red-dye mixture dispersed in 2 percent aqueous surfactant, using a V-7 "Lightnin" mixer for 20 min at maximum shear, in a 250-ml stainless steel beaker. The slurry was filtered through a 100-mesh stainless steel screen. The resultant solids content was 15.5 percent. Density was 1.03 g/cm^3. No attempt was made to recover or wash the remaining solids through the screen at this point in the development process. The addition of the dye slurry occurred uniformly and predictably. The dispersion settled slowly and showed a low shear-dependency relative to higher concentration thixotropic slurries that were also prepared. Rates of addition were varied from 2 to 8 cm^3/min. The total quantity of slurry introduced over an 18-min period was 58 cm^3. This time period resulted from material limitations, since only 10 g of dye powder remained in reserve when the series was run. Consequently, no attempts to optimize the process were possible. Experimental details are given below:

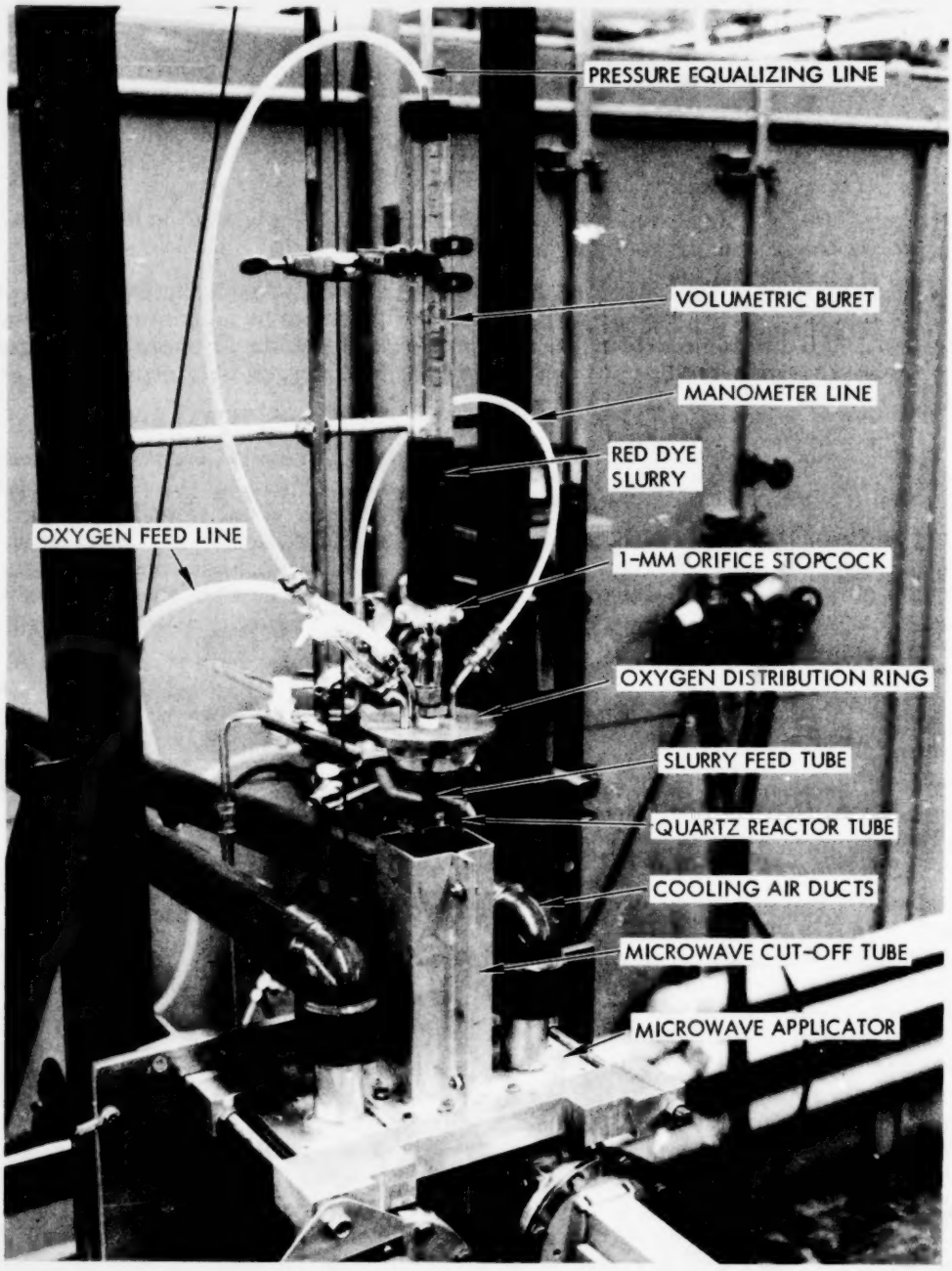

Figure 3. Red dye slurry feed system.

- Run No.: 68-58
- Applicator: Series C, 0.6-liter reactor volume
- Microwave Power: 4.6 kW
- Maximum Feed Rate (not optimized): 494 g/hr slurry, 87 g/hr equivalent solids
- Pressure Range: 35-60 torr
- Oxygen Flow: 300 liters/hr
- Packing: Quartz Raschig rings: 25% 0.4 by 0.8 mm, top zone; 75% 0.8 by 0.8 mm, bottom zone
- Conversion: 99.99%, based on starting material, which reacted to form a mixture of gases and a solid residue

The principal effluent gases were CO_2, CO, and H_2O. The nitrogen oxides which were expected were not observed because of a 2 to 3 part per thousand limit of sensitivity in the mass spectrometer.

Samples were collected at three trap positions downstream from the plasma. Methylene dichloride was used to dissolve the residues. A blank or control run was performed preliminary to the detoxification sequence. Based on the weight of starting material, the unknown solid residue, which was detected in the receiver, measured less than 0.2 percent.

Spectrophotometric comparisons in the visible region of a methylene dichloride solution of the unknown solid, and known concentrations of the initial dye mixture in the same solvent indicated that not more than 5 ppm of the starting dyes had passed through the plasma. Polyaromatic hydrocarbons were not detected above 2 ppm, using an automatic GC/MS data system. The less than 0.2 percent reddish-brown residue showed via IR and GC/MS the additional presence of dioctyl phthalate, silicone materials, and benzene traces, which probably entered the analytical samples during the CH_2Cl_2 washing of the traps and connective tubing.

In Fig. 4, an infrared scan of the residue on a Perkin Elmer 621 spectrophotometer is shown. A Finnegan Model 4021 was used for the GC/MS data system analysis of the same residue.

UV fluorescence from the residue was negative, using a 2537 Å Pen Ray quartz lamp source, whereas 10 of 12 PAH compounds suggested by NWSC, Crane, Indiana, as possible oxidation products of the dye mixture luminesced brightly. Two of the 12 compounds did not fluoresce and, subsequently, were scanned in the ultraviolet after dissolving in methylene dichloride solution. Their reported spectral peaks differed significantly from that of the residue in the same solvent. Table 2, Part I, is a list of these compounds and their ultraviolet response to 2537 A UV exposure.

Ultraviolet spectrophotometric scanning of the residue dissolved in methylene dichloride showed no absorption peaks that could be attributed to PAH compounds with known maxima. A listing of additional PAHs in Table 2, Part II was obtained

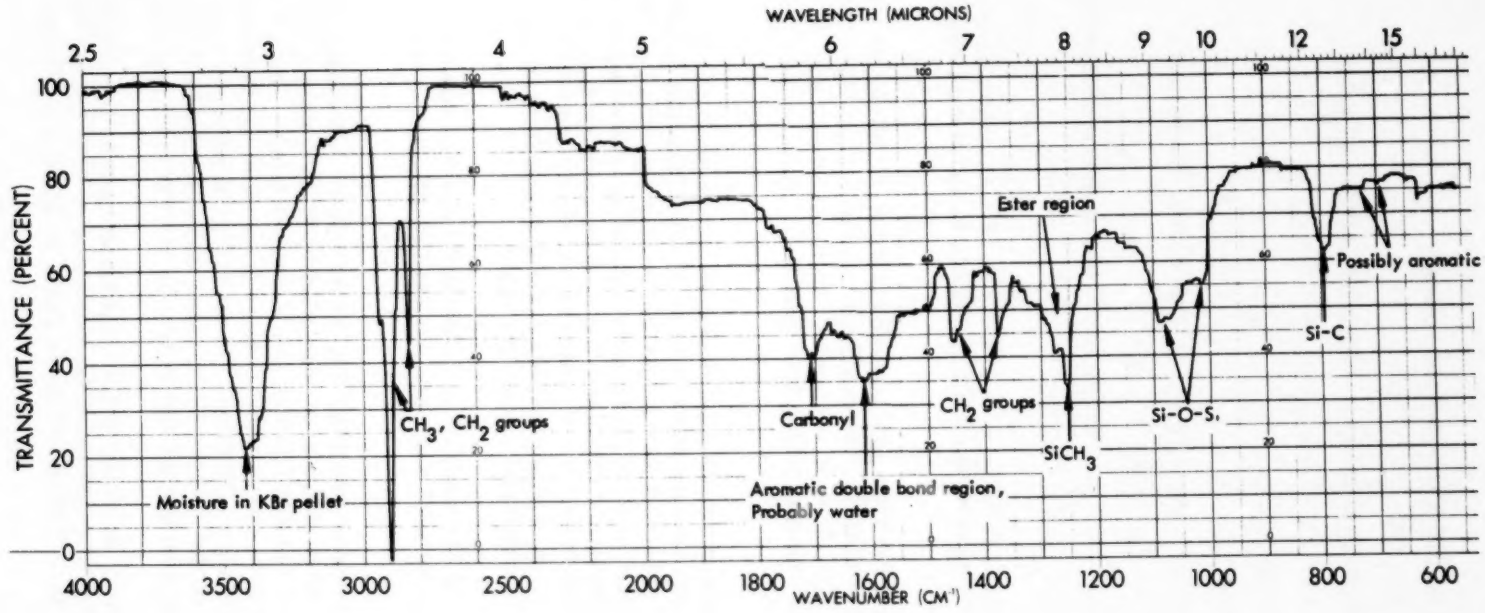

Figure 4. Infrared scan of solid residue from oxygen plasma reactor.

from Ref. 5. Since PAHs have been found in air oxidation products derived from these materials,[6] a significant advantage would appear to derive from the plasma process.

TABLE 2. POLYAROMATIC COMPOUNDS AND THEIR 2537 Å ULTRAVIOLET FLUORESCENT RESPONSE AND ABSORPTION MAXIMA

Compound	Visible Fluorescent Response to 2537 Å UV	UV Absorption Maximum (μm)
Part I		
Anthracene	+ (yes)	254
Benzo-a-phenanthrene	+	297
Benzo-d, e, f-phenanthrene	+	....
Benzo-a-pyrene	+	....
Chrysene	+	270
Decacyclene	- (no)	....
1,2,3,4 - Dibenzanthracene	+	....
1,2,5,6 - Dibenzanthracene	+	299
9,10 - Dimethylanthracene	+	....
7,12 - Dimethylbenz-a-anthracene	-	....
9,10 - Dimethylbenz-a-anthracene	+	258
1-Methylnaphthalene	+	280
Part II		
Phenanthrene		295
Pyrene		338
Fluoranthene		289
1,2 - Benzanthracene		290
3,4 - Benzopyrene		270
Perylene		334
Anthanthrene		441
1,12 - Benzoprylene		435
Coronene		388

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3. Ref. 2, p. 7.

4. Brown, L. C. and A. T. Bell, "Kinetics of the Oxidation of Carbon Monoxide and the Decomposition of Carbon Dioxide in a Radiofrequency Electric Discharge," Ind. Eng. Chem. Fund, Vol. 13, Mar 1974, pp. 203 - 18.

5. Leithe, W., The Analysis of Air Pollutants, Trans R. Kondor, Ann-Arbor-Humphrey Science Publishers, Ann Arbor, Michigan, 1970, p. 260.

6. Ref. 2, p. 12.

Appendix

CHRONOLOGICAL DEVELOPMENT OF FEED TECHNIQUES

A.1 METHANOL-WATER MIXTURE

The first mixtures that were prepared contained 15 to 20 percent solids in 50/50 wt% methanol-deionized water solutions. Introduction to the plasma zone was by way of two feed methods – a 1-liter pressure-equalized volumetric dropping funnel and a 250 cm^3 volumetric dropping buret which was open to the atmosphere at the top. Methanol was used, since it wetted and dissolved a large amount of dye, but would not consume a disproportionately large amount of oxygen in the plasma reaction. Water was used in combination with methanol in order to minimize the oxygen demand of the solvent. The 50/50 proportion was, from a handling standpoint, an efficient combination, because the solids settled extremely slowly while waiting for the feed step to start after filling the reservoir of the buret or funnel.

During the addition of these mixtures, however, the dissolved dye components and the slurry solids clogged the orifices of both feed devices. This was caused by rapid evaporation of the methanol solvent component of the system as the liquid passed from bulk form into droplets in the reduced-pressure environment. The contention that the clogging was increased by the presence of agglomerated solids in the slurry indicated that this combination would probably not be satisfactory under any conditions and, thus, was removed from further serious consideration.

A.2 POWDERED SOLIDS

A.2.1 Laboratory Model Continuous Solids Feeder

A first generation solids feed method was constructed to introduce materials into the plasma zone via gravity fall. Figure A-1 is a schematic drawing of the unit. Figures A-2 and A-3 are photographs that illustrate the device positioned above the reactor. Not shown in the drawing are relief valves and pressure-equalizing connections between the lower chamber and the belt-feed area.

Tests under vacuum, as well as atmospheric pressure, showed that for granular, free flowing solids, the system worked very well. For non-free-flowing powders, however, "bridging" and "ratting" occurred in the lower chamber. The use of a "Vibro-Graver" vibrator (Burgess Vibrocrafters, Inc., Model V-73), in which the side of the vibrator shaft was placed against the outside handle of the lower powder transfer valve, produced an immediate improvement but did not solve the problem completely. Powder feed rate was low, but acceptable on an interim basis. Throughput was about 1/2 kg/hr (1 lb/hr).

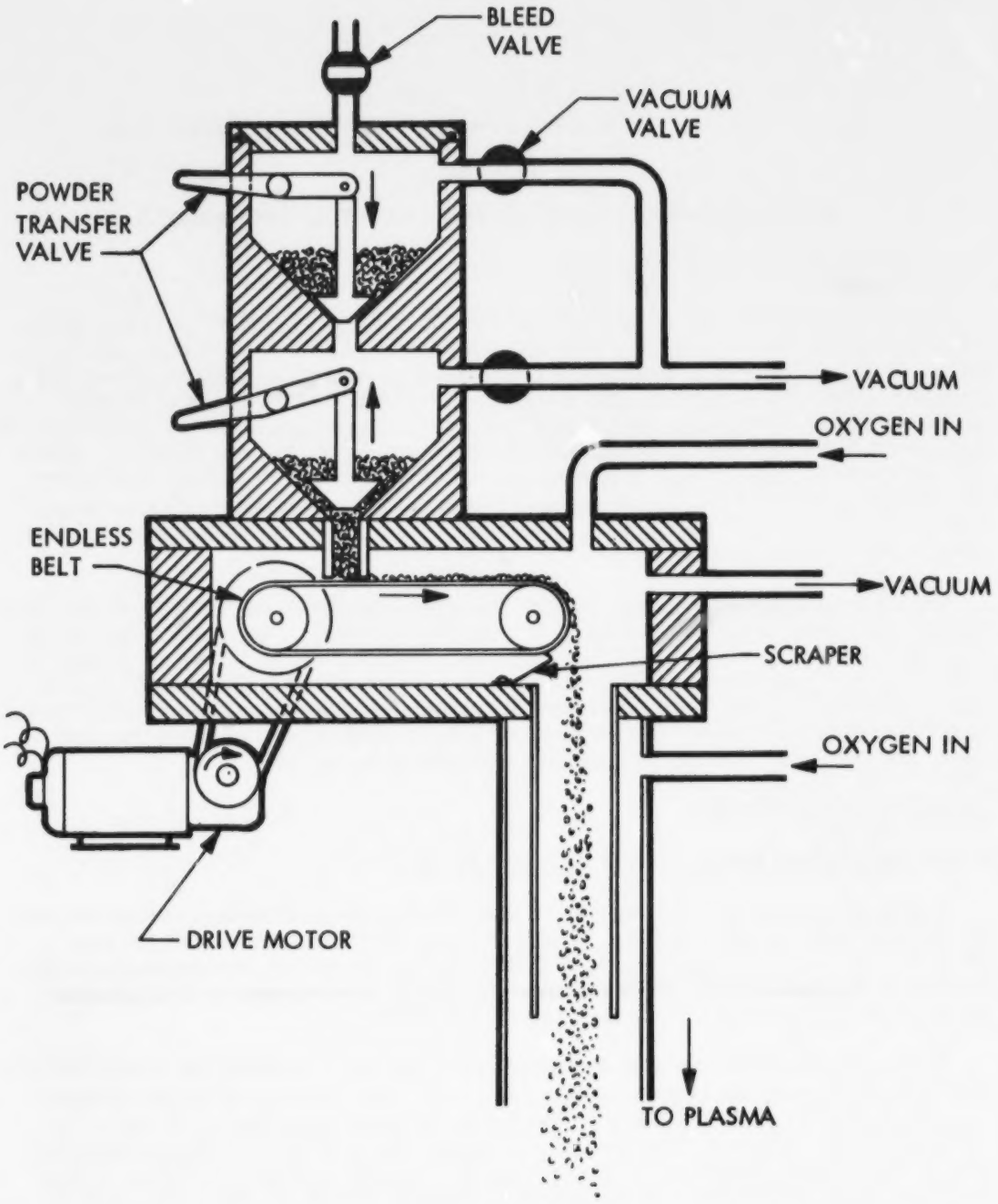

Figure A-1. Schematic of solids feed system.

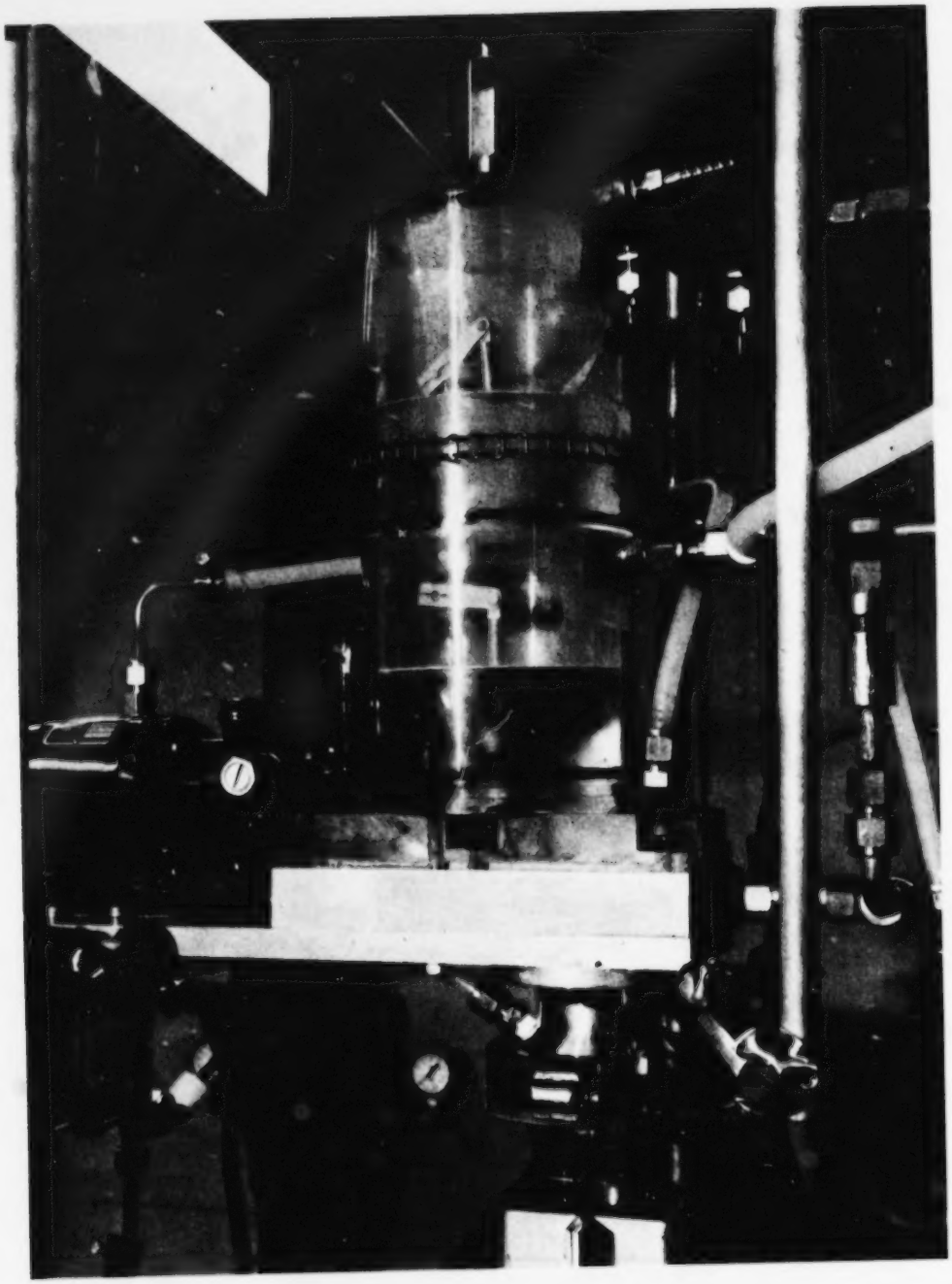

Figure A-2. Solids feed system, close up.

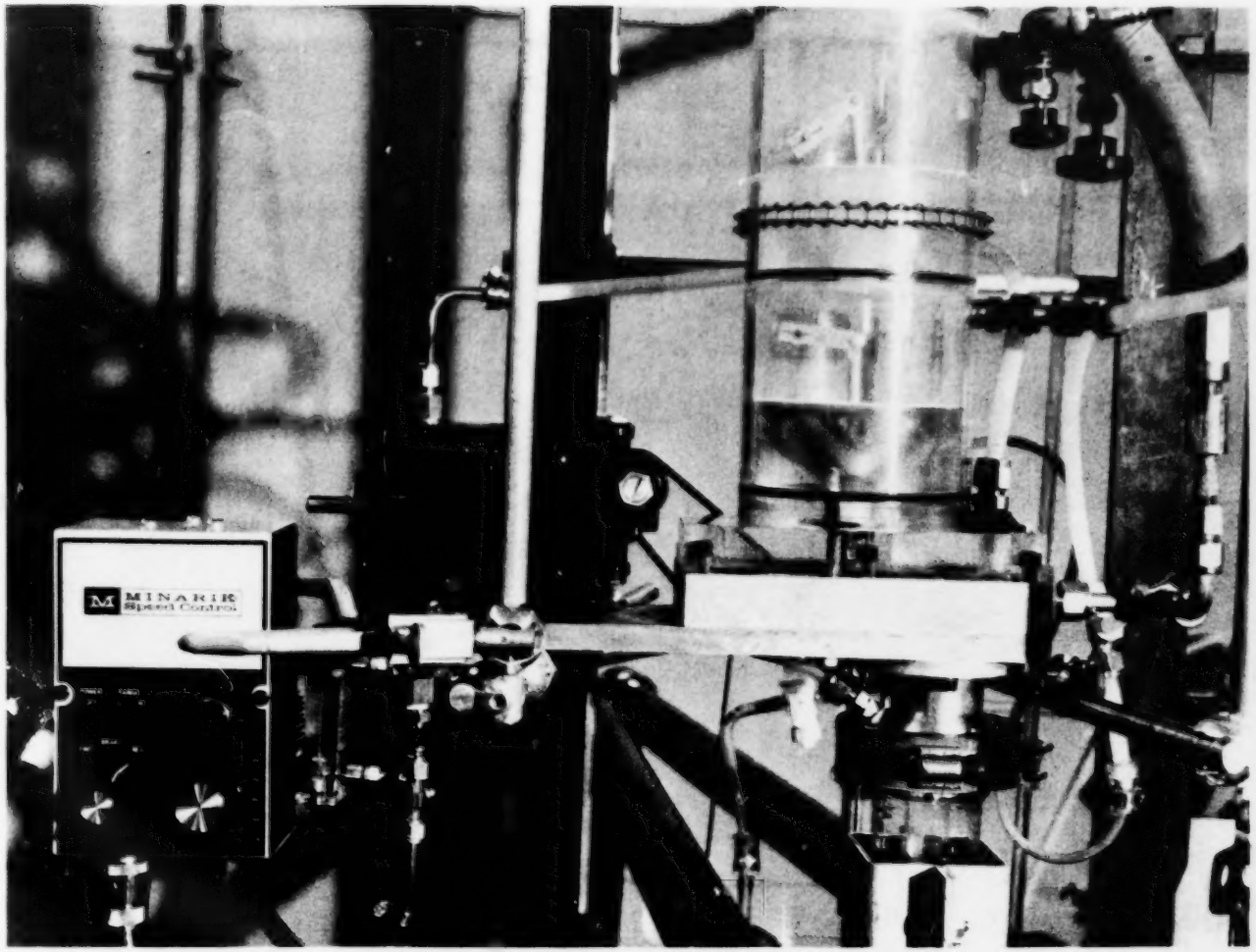

Figure A-3. Solids feed system, front view.

To minimize "ratting" etc., in the test powder, which was a non-free-flowing mixture, the powder was pressed into 7.6 cm (3 in.) diameter cakes at about 15,000 psi, then crushed and sieved through an 80-mesh screen. The particles smaller than 80 mesh – now essentially free-flowing – could be added via the endless belt technique. Because of their large size as compressed agglomerates, however, a second problem developed which appeared, initially, to be related to a nonhomogeneous addition rate. However, it was later surmised that the larger particles upon contacting the plasma zone, decomposed very rapidly in the usual manner, resulting in development of significant pressure differentials between the vacuum feed chambers and the lower plasma reactor. As a result, the powder particles, in the process of falling under gravity or during decomposition, were also drawn upward toward the feed chamber, producing a whirlwind phenomenon with attendant, unpredictable changes in the amount of material falling onto the belt, and consequently, off the belt into the plasma. The results of this method were readily apparent in the tarry products which had not even "seen" the plasma decomposition zone. To solve this problem, it will be necessary to install larger-diameter pressure-equalizing connections between the feed and the reactor chambers, and increase the construction angles of the hopper chambers.

During another powder feed sequence in which the original noncompacted powder was being drop fed into the plasma, some air leaks developed in the feed system. Although the run was otherwise acceptable, the presence of air precluded the reaction products from being considered as valid samples for analysis. Since air-plasma reactions result in NO, and probably NO_2, these NO_X products could react with the dye as it passed through the plasma zone or with the plasma effluent gases further down stream. These nitrogen-containing materials would be nonreproducible and, more importantly, nonrepresentative of oxygen plasma reactions.

A.2.2 Pressed-Cake Batch Process

In another series of exploratory runs, small 2.5 cm (1 in.) press cakes were treated in the plasma. The discs were formed at 1,000 psi, and placed in the reactor above the Raschig ring section. The resultant cake breakup and plasma reactions were also uneven. It was postulated that a much more rapid decomposition of the easily decomposed sugar component (20 percent of the mixture) occurred in comparison with that of the aromatic dye components. Since the microwave plasma is routinely started at 10-torr oxygen pressure, the physical breakup of the press cake, and concomitant rapid powder flash-through, could have occurred prematurely, i.e., before addition of the oxygen could be made to increase pressure to the required levels adequate for detoxification. These phenomena – inadequate oxygen and nonuniform cake breakup – are related directly to batch processing and would not be expected to occur in a continuous feed system.

In the above context, attention is called to the successful press-cake decomposition described in the Special Report, Microwave Plasma Detoxification of Kepone Pesticide, May 1976. In these tests, the press cakes (80% Kepone, 20% clay) decomposed uniformly and cleanly in the plasma environment. The relative simplicity in the number of organic compounds of the Kepone mixture, relative to the Navy dyes, may have contributed to this difference. In addition, Kepone, when treated, sublimes from a solid powder directly to the vapor state, and would be expected to react very rapidly in the gas phase. However, the organic dye mixture components (two aromatic dyes, sugar, carbon) will melt, decompose, and/or carbonize before reacting in the plasma,

and only slowly under these batch conditions because of the large particles present in the mass of the charred material. It is probable, therefore, that sublimation was a principal cause of the extremely rapid and, therefore, favorable reactions which are noted above for the Kepone–oxygen plasma detoxification.

Further in-house development was not pursued for two reasons: (1) commercially available feeders were scheduled for acquisition during Phase III of the current program and (2) development of a rotating or vibrating reactor, plus reactor-internals (packings), will be necessary in order to develop the needed capability for variable residence time in the reactor. This is also part of Phase III.

A.3 METHYL ETHYL KETONE SOLUTIONS

In this system, MEK was used as solvent per recommendations from NWSC, Crane, Indiana. Mixtures, typically 40-g red dye mixture and 80-g MEK, were prepared and allowed to stand overnight, or mixed 1 to 2 hr. The resultant solutions were filtered and used for the plasma reaction tests. In all cases, the tip of the dropping funnel clogged before the dye could reach the plasma. Since it became obvious, after the fact, that the clogging was related to deposits at the orifice which occurred when the solutions evaporated, lower, 13 to 15 percent concentrations were prepared. These solutions passed through the feeder with no difficulties, and were detoxified with no red colorations or deposits visible below the reactor. The products detected by MS were CO_2, CO, and H_2O. Nitrogen oxides were expected, but these were below detectability because of a 2 to 3 parts per thousand sensitivity in the mass spectrometer. However, each mole of MEK, which made up 85 to 87 percent of the solution consumed 110 to 130 liters of oxygen as it passed through the plasma. This was counter-productive for both the solvent and the oxygen plasma gas, indicating that essentially any solvent system that is added purposely will result in an uneconomic operation of the process. This led subsequently to preparation of aqueous dispersions as a feed vehicle, which led to the successful introduction and detoxification reaction for the dye mixture. Details of this development are presented in the next section.

A.4 AQUEOUS DISPERSIONS

Since the red dye components as a mixture were essentially hydrophobic or non-water wetting, the initial effort involved obtaining wetting agents/surfactants which would yield hydrophilic or water-wettable dispersions. The silica gel and carbon black were expected to wet reasonably well, whereas the two dye components, xylene azo-β-naphthol and 1-methyl-aminoanthraquinone, were the principal hydrophobic components. The sugar, of course, dissolved on wetting. In consultation with NWSC personnel, several surfactants were suggested in addition to those on hand at LPARL. A series of tests was then run by mixing tenth-gram samples with 2 percent solutions of the surfactants and visually determining the results of enhanced wetting. The best agent was used to prepare concentrated slurries using a V-7 "Lightnin" mixer as a medium-to-high shear agitator. Stability in suspension was also evaluated on a visual basis. A list of the agents tested is given in Table A-1.

A nonionic surfactant, TEC 1216 E, yielded the most readily wetting, stable suspension at 25 to 30 wt% solids. This agent is reported by Rohm and Haas to be very similar to their Triton N-101 nonionic surfactant, which is a water-soluble nonyl phenoxy polyethoxy ethanol containing 9 to 10 moles of ethylene oxide.

TABLE A-1. SURFACTANTS TESTED FOR PREPARATION OF AQUEOUS RED DYE DISPERSIONS

Trade Name	Source	Type	Chemical Identity
TEC 1216 E	TEC Chemical Co.	Nonionic	Ethylene oxide nonylphenol
Ethoquad C/12	Armour Industrial Chemicals	Cationic	Methylbis (2-hydroxy ethyl) cocoammonium chloride
Roccal 10%	Winthrop Labs	Cationic	Alkyl ($C_{18}H_{17}$ - $C_{18}H_{37}$) dimethyl benzylammonium chloride
Aerosol OS	American Cyanamid	Anionic	Sodium isopropyl-naphthalene sulfonate
Aerosol OT	American Cyanamid	Anionic	Sodium dioctyl-sulfosuccinate
Aerosol GPG	American Cyanamid	Anionic	_____
_____	Matheson Coleman and Bell	Anionic	Sodium lauryl sulfate

Various formulations of the dye in the TEC 1216 solution were added through a dropping funnel inserted above the plasma zone. The funnel was used at atmospheric pressure above the slurry. In all instances, using different stopcocks, orifices, valves, etc., the slurry flow was such that excessive amounts entered the reactor as the result of plugging and deplugging of the orifices. These instantaneous plug breakthroughs were large, on the order of 5 to 10 cc/s (40 to 80 lb/hr), which obviously exceeded the oxygen supply in the reactor, causing untoward, excessive contamination in the quartz reactor. It was determined next that when the slurry was added with reduced pressure above the feed that plugging was minimized. It was this modification which, in combination with other variables, permitted successful feed of the dye dispersion. The investigative steps are described below listing the methods used for solving the non-Newtonian (thixotropic) flow and other problems associated with feed procedure. A photograph of the new feed system is shown in Fig. 3, Section 4.

The following variables were studied in this connection.

- The pressure head above the buret stopcock was minimized by decreasing the height of the slurry. This included equalizing the pressure above the slurry to approximately that of the reactor through the use of flexible tube connections.

- A precision oxygen feed-ring for uniform gas addition into the reactor was designed, machined, and operated successfully.

- The feed stopcock orifice size was optimized at 1 mm diameter. Less than 1 mm resulted in clogging. Greater than 1 mm resulted in an excessive introduction rate which was significantly more than 10 lb/hr. The stopcock was constructed from Teflon in order to obviate the need for stopcock lubricant. When grease was used for the 1-mm orifice stopcock, clogging occurred. It was necessary that the stopcock also be vacuum tight (approximately 1 torr) to avoid nonuniform bubbling and frothing within the slurry.

- The glass feed-line tube between the stopcock and the reaction zone was constructed to have a diameter significantly greater than the buret tip internal diameter. The tube was cleaned with laboratory glassware detergent ("Alconox") to produce a water break-free surface to avoid nonuniform drop formations within the tube. The tube end was cut 45 deg to minimize the size of the drops. The position of the feed tube within the microwave cutoff was optimized to prevent spattering and/or overheating within this zone, which, if not prevented, could result in excessive evaporation and clogging at the tip.

The optimum slurry was developed from a number of trial dispersions: A 20 percent red dye mixture was dispersed in a 2 percent TEC 1216E surfactant solution using a V-7 Lightnin mixer for 20 min, with maximum shear/agitation in a stainless steel beaker. The slurry was filtered through a 100-mesh stainless steel screen (nominal 150 μm openings). The resultant solids content was 15.5 percent. Density was 1.03 g/cm^3. The dispersion settled slowly and showed minimum thixotropy relative to 30 percent slurries also prepared.

The above techniques, concentrations, etc., were developed specifically for gravity-flow feeding for the current plasma reactor. It is important to note, however, that because of the complex design required for gravity-flow introduction, the forthcoming Phase III methods will utilize positive displacement feed techniques for liquids, dispersions, and related materials to obviate the requirement for these time-consuming engineering developments.